ESTIMATION OF EXPOSURE OF PERSONS IN CALIFORNIA TO PESTICIDE PRODUCTS THAT CONTAIN MOLINATE

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ABSTRACT

Molinate is a selective herbicide that is used exclusively on rice in California. It is applied predominantly by air as a granular formulation. There have been 12 reported illness/injury cases that were associated with exposure to molinate alone or in combination with other pesticides from 1982 to 1992 in California. Following ingestion, molinate is readily absorbed, metabolized, and excreted in animals and humans. Workers involved in loading molinate were identified as having the greatest potential for exposure. Worker exposure studies show that the exposure to workers loading molinate has consistently been in decline for the last 15 years as additional personal protective equipment, engineering controls, improved formulation, worker training, and use restrictions have systematically been implemented. This report was prepared as part of the Department's risk characterization document for molinate because molinate reproductive toxicity and neurotoxicity studies have shown possible adverse effects in exposed laboratory animals.

HUMAN PESTICIDE EXPOSURE ASSESSMENT

California Environmental Protection Agency
Department of Pesticide Regulation
Worker Health and Safety Branch

MOLINATE

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Introduction

Molinate is on the list of the first 200 products to be reviewed under the California Birth Defect Prevention Act of 1984 (SB-950). Studies with molinate have shown possible adverse reproductive and neurotoxicity effects in laboratory animals. A human exposure assessment was prepared for molinate on December 5, 1989 and was revised prior to each growing season since that time. Since the initial studies in 1980-81, several additional molinate worker exposure monitoring studies have been conducted. This revision of molinate human exposure assessment includes exposure studies conducted following the previous revision. Human exposure assessment provides essential information for the risk assessment of pesticides. This human exposure assessment document will be an integral part of the Risk Characterization Document of the Department of Pesticide Regulation (DPR) for molinate. It will also serve as a basis for developing mitigation strategies if exposure to molinate is found to cause excessive risk.

Chemical and Physical Properties

Molinate (CAS # 2212-67-1) is the common name for S-ethyl hexahydro-1H-azepine-1-carbothioate. Molinate has a molecular formula of $C_9H_{17}NOS$ and a molecular weight of 187.3 g/Mol. It is a liquid at normal temperature and pressure and slightly soluble in water but miscible in common organic solvents. Molinate has a boiling point of 202^{o}C and a vapor pressure of 5.0 x 10^{-3} mm Hg at 25^{o}C (Myers, 1987; 1988; Stauffer, 1971). Its half-life in soil is 28 days (Lay, 1990). Molinate is a selective herbicide that is used for control of weeds in rice fields.

Regulatory Status

The Department of Pesticide Regulation has issued an interim risk characterization document each year from 1990 to 1994, recommending consecutive exposure mitigation measures to minimize the exposure of workers handling molinate in California. The Department also required additional worker exposure monitoring studies to better define the potential exposure of workers to molinate. The mitigation measures included personal protective equipment (PPE), engineering controls, worker training, use restrictions, and restriction on the amount handled by workers. The additional mitigation measures were implemented through Worker Safety Permit Conditions issued prior to each rice growing season.

Formulations

Ordram® 8E and Ordram® 10G are the only two molinate-containing products registered in California. Ordram® 8E is an emulsifiable concentrate formulation with 90.9 percent active ingredient (a.i.) and contains 8 pounds (lb) a.i. per gallon. Ordram® 10G is a granular formulation that contains ten percent a.i.

Usage

Molinate is a selective herbicide that is used exclusively on rice in California for control of barnyardgrass. The application rate for Ordram® 10G is 3 to 5 lb a.i. per acre and for Ordram® 8E is 3 lb a.i. per acre. Ordram® 10G is applied either by ground or air equipment. Ordram® 8E application is allowed only by ground equipment in California (see attachment I). The majority of molinate used in California is applied by air, using the granular formulation. A total of 1,387,600 lb of molinate was applied to 350,990 acres of rice fields in California in 1992 (DPR, 1994a).

Label Precautions

Both Ordram® 8E and Ordram® 10G are toxicity category II pesticides carrying "Warning" as a signal word. Aerial application must be made only when the wind velocity is ten miles per hour or less. The latest molinate worker safety permit conditions (1994) require personal protective equipment (PPE), engineering controls, and training for workers handling molinate. Attachment I is a copy of the 1994 permit conditions. The application of Ordram® 8E by air is not allowed in California according to the permit conditions.

Human Illnesses and Injuries

There have been 12 reported illness/injury cases that were associated with exposure to molinate alone or in combination with other pesticides from 1982 to 1992 in California (DPR, 1994b). From 1982 to 1985, no molinate-associated illnesses or injuries were reported. The 12 reported cases occurred from 1986 to 1992. Of the 12 cases, six were systemic, three were eye injuries, and three were skin injuries.

Dermal Irritation/Sensitization

Technical molinate is a mild to moderate skin and eye irritant in the rabbits. Dermal irritation studies with formulated molinate in rabbits at 0.5 g/animal showed no effect or slight erythema at 24 hours. The symptom appeared to be transient and subsided by 72 hours (Stauffer, 1968). Molinate formulations did not cause sensitization in guinea pigs (Mutter, 1986).

Metabolism

Simonsen albino rats were administered a single (72 mg/kg) gavage dose with ^{14}C-labeled molinate in two studies (DeBaun, *et al*., 1987a; DeBaun, *et al*., 1987b). The first study consisted of two parts: a mass balance and tissue residue. Urine, feces, air, tissues and cage washes were collected from two rats of each sex. By 72 hours post-exposure, 82.1, 10.6, 5.8, and 0.9 percent of the dose were recovered in urine, feces, cage wash, and exhaled air, respectively. Tissue distribution of the ^{14}C-labeled molinate was observed in six rats of each sex. Blood and liver had the highest residues. In the second study, thin-layer chromatography, NMR, and mass spectral analysis were used to identify urinary metabolic products. Urine samples were the composite of the first 48 hours of output. Molinate mercapturate (35.4 percent of urinary radioactivity), 3- and 4-hydroxy molinate glucosiduronic acid (26.1 percent), hexamethyleneimine (14.6 percent), and 3- and 4-hydroxy hexamethyleneimine (10.3 percent) were the major metabolites and accounted for 86.4 percent of ^{14}C found in urine. The primary metabolic pathways of molinate were sulfoxidation, glutathione conjugation, and ring hydroxylation.

In a series of studies (Ritter *et al*., 1991; Ritter, 1991a; Peffer, 1991; Ritter, 1991b), Sprague-Dawley rats were given a single low dose gavage, 14 days gavage, a single high dose gavage, or a single intravenous dose of ^{14}C-labeled molinate (94.2 - 96.7 percent purity, 17.5 mCi/mmol). Most of the radiolabel (64-85 percent) was excreted in the urine in these studies within 36 hours. Radiolabel in feces ranged from 2.5 to 14 percent of the dose. Molinate mercapturic acid was the major metabolite, accounting for 21.2 to 51.3 percent of the administered dose in these studies. Other metabolites were 3- and 4-hydroxy molinate glucoronide, hexamethyleneimine, 3- and 4-hydroxy hexamethyleneimine, 4-keto hexamethyleneimine, hydroxy molinate mercapturic acid, and 3- and 4-hydroxy molinate, each accounting for 0.5 to 15 percent of the dose.

Male Cynomolgus monkeys (4/dose) were administered ^{14}C-molinate (99.9 percent purity) either by gavage at 6 mg/kg or 60 mg/kg, or intravenously at 6 mg/kg (Lythgoe *et al*., 1992). Monkeys receiving an i.v. injection excreted in the urine 87.4 percent of the administered dose during the first 24 hours and 95.8 percent of the administered dose within 192 hours. Total recovery was 97.5 percent of the administered dose. <u>The major urinary metabolite was the glucuronide conjugate of 4-hydroxy molinate (33.3 percent)</u>. Other metabolites were cysteine conjugate of molinate (11.7 percent), molinate mercapturate (10.2 percent), the glucuronide conjugate of 3-hydroxy molinate (4.7 percent), the methyl ester of glucuronide conjugate of 4-hydroxy molinate (2.4 percent), the acetic acid conjugate of molinate (3.2 percent), the glucuronide conjugate of ring hydroxylated molinate (1.9 percent), hexamethyleneimine (0.7 percent), and 4-hydroxy molinate (0.3 percent). The identified metabolites accounted for 68 percent of the urinary radioactivity. Monkeys administered a single oral dose at 6 mg/kg excreted 48 percent of the administered dose in urine in 24 hours. During the following seven days an additional 2.3 percent was excreted in urine. Total recovery was 51.1 percent of the administered dose despite the analysis of feces. Monkeys administered a single oral dose at 60 mg/kg excreted 79 percent of the administered dose in urine in 24 hours. In the following seven days an additional 1.2 percent was excreted in urine. Excretion in feces accounted for 1.8 percent of the total dose in eight days.

Human volunteers (six) were given a single oral dose (5 mg) of molinate (99.7 percent purity) in corn oil (Batten *et al*., 1992). The major metabolite was 4-hydroxy molinate. Peak excretion of 4-hydroxy molinate occurred within the first four hours and was almost complete by 24 hours. An average of 39 $\pm$ 9.7 percent of the administered dose was excreted in the form of 4-hydroxy molinate in the urine by 24 hours. Molinate mercapturate urinary excretion accounted for 0.9 $\pm$ 0.35 percent of the administered dose in 24 hours. Human metabolism of molinate appears much more similar to monkeys than to rats. Molinate was detected in some blood samples collected after 0.5 to 1.0 hour of dosing but the concentrations were close to the limit of detection of 1 ng/mL.

Following ingestion, molinate is readily absorbed, metabolized, and excreted in animals and humans. The primary urinary metabolite in humans is 4-hydroxy molinate. The primary metabolite, 4-hydroxy molinate, is a viable exposure indicator that can be used in monitoring human exposure to molinate.

Dermal Absorption

The dermal absorption of molinate has been studied in rats and *in vitro* in humans. Dermal absorption (i*n vivo*) of ^{14}C-molinate was determined in dorsally shaved Charles River Sprague-Dawley rats (Holmes, 1990). Five to six rats per dose level (0.61, 1.39, and 10.6 mg/kg) were administered ^{14}C-molinate dissolved in methanol and placed into individual metabolism chambers. The majority of rats had the treatment site covered with an occlusive wrap which was kept on for 24 hours until the site was washed. One group of rats dosed at 1.39 mg/kg did not have the treatment site occluded and were exposed for seven hours prior to washing. All rats remained in metabolism chambers for 72 hours. At sacrifice, radiocarbon was quantified in carcass, urine, feces, exhaled air, and treatment site.

Absorption in the occluded rats was uniform across dosages (56.0 $\pm$ 3.0 percent) and recovery of radiocarbon was complete (97.3 $\pm$4.5 percent). Radiocarbon recovery was 80.6 $\pm$ 7.0 percent in the unoccluded rats and the absorption, when corrected for recovery, was 47.1 percent.

In a separate *in vivo* dermal absorption study, rats were administered 0.1, 1.0, or 10.0 mg of molinate (as molinate in solution) or 1.0 mg of molinate (as an Ordram 15G surrogate using kaolin clay carrier) (Little, 1991). All molinate formulations used ^{14}C-molinate. The application site was protected with an activated charcoal filter patch to trap volatilizing molinate. Material was left on the skin for the duration of the study (up to 120 hours) for all except the Ordram surrogate which was washed after 10 hours. The surrogate was also applied dry to the skin. Urine, feces, cage wash, filter patch, and carcass were analyzed for radiocarbon. A dermal absorption of 53 percent in 24 hours was estimated based on this study (Thongsinthusak, 1991).

The Department (Thongsinthusak, 1991) reviewed an *in vivo*/*in vitro* rat and *in vitro* human dermal absorption study (Scott, 1991) and an *in vitro* rat and human dermal absorption study (Scott and Clowes, 1991) to make an estimate of *in vivo* human dermal absorption. The Department derived a ratio of *in vitro* rat to *in vitro* human (average ratio = 5.2) dermal absorption and divided the *in vivo* rat (53 percent absorption) by that ratio to estimate an interim *in vivo* human dermal absorption. The estimated human *in vivo* dermal absorption of 10.2 percent was conditionally accepted for regulatory purposes pending a confirmatory human *in vivo* dermal absorption study to be submitted in 1992. No confirmatory human *in vivo* dermal absorption study has been submitted to the Department, therefore, a dermal absorption of 53 percent will be used in this document based on rat *in vivo* dermal absorption rate.

Dislodgeable Foliar Residue

Because of the nature of rice growing and mechanized harvesting, dislodgeable foliar residue data to determine the exposure to field workers are unnecessary.

Worker Exposure

Several molinate worker exposure studies have been conducted over the years. The earlier studies were conducted using passive dosimetry (pad or t-shirt, hand wash, air sampling). The later and most recent studies were conducted using biological monitoring.

Maddy et al. (1982) monitored dermal and inhalation exposure of one pilot, two loaders, and two flaggers handling Ordram® 10G (packaged in 50-lb bags) during aerial application to rice fields. The workers were monitored during two workdays. The application rate was 4 lb a.i. per acre. Air samples were taken from the breathing zone of workers, using XAD-4 filters, assuming all airborne residues were in vapor phase. Hand exposure was measured using distilled water hand washes. Durham and Wolfe-type patch dosimeters were attached to the exterior of coveralls or clothing at various body parts to measure potential dermal exposure. No spiked samples were taken to determine field recoveries.

The loading procedure during this study was substantially different from that currently in practice. One loader would toss a 50-lb bag onto the sawtooth blade welded along the hopper cover screen. And the other loader would pull the bag along the blade, hemisecting the bag and emptying the contents into the hopper. Once the hopper was full, it was positioned over the plane and the contents were transferred into the plane's holding tank. Each hopper contained 1,600 lb of Ordarm® 10G (32 bags) and required ten minutes per loading cycle. The pilot was not involved in loading. Flaggers were sometimes subject to accidental application. Workers wore a long or short-sleeved shirt, long pants, shoes, and coveralls. The coveralls were provided by the investigators for monitoring purposes.

Knarr (1980) monitored the exposure of workers applying either Ordram® 10G at 3 to 5 lb a.i. per acre or Ordram® 8E at 1 lb a.i. per acre by air in Arkansas. The exposure monitoring techniques and the work tasks were similar to the study conducted by Maddy *et al.*, 1982. Two additional pads were placed under the coveralls to establish a clothing penetration factor. Penetration factors of 53 and 30 percent were estimated for the 10G and 8E formulations, respectively. Analytical recoveries for laboratory and field spikes were 95 percent or more for the 10G formulation and 80 to 117 percent for the 8E formulation. Results were adjusted for laboratory recoveries.

The estimates of exposure for pilots, flaggers, and loaders handling the 10G formulation in Table 1 are based on both Maddy *et al*., 1982 and Knarr, 1980 studies. In Maddy *et al.* (1982), more than 85 percent of dermal dosimeter samples for pilots and flaggers contained no detectable residues. The minimum detection limit (MDL) was not reported and was assumed to be the lowest value reported (0.01 ug/cm^2). Samples with no detectable residues were assumed to contain residues one-half the MDL.

Table 1
The Estimate of Exposure of Pilots, Flaggers, and Loaders
Handling Ordram® 10G

Work Task (n)	Head +Neck	Potential Body*	Hand	Inhalation	Absorbed Daily Dosage (ADD)
	ug/4-hours	ug/4-hours	ug/4-hours	ug/4-hours	ug/kg/4-hours
10G:					
Pilot** (5)	37.3	629.6	15.8	121.4	3.5
Flagger (8)	66.8	1597.0	20.5	55.8	10.5
Loader (12)	1752.3	35154.9	662.2	3323.6	201.1
8E:					
Pilot** (4)	29.8	763.3	5.4	32.5	2.4
Flagger (4)	2627.5	56777.8	60.1	290.5	174.4
Loader (8)	249.5	25071.6	163.4	135.3	87.3

All data are geometric means (log-normally distributed).
n - Number of replicates.
* - Total exposure to the body.
** - The pilot who routinely assisted loaders filling the plane in Knarr, 1980 study was excluded.
Based on: Male pilots and loaders, female flaggers, clothing of long-sleeved shirt, long pants, and shoes. Body weight, body surface area, and inhalation rates from Thongsinthusak *et al*., 1993. Normal clothing penetration of 53 and 30 percent for 10G and 8E formulations, respectively (Knarr, 1980), dermal absorption of 53 percent (see Dermal Absorption section), and inhalation uptake of 50 percent (Raabe, 1987).

The estimates of exposure for pilots, flaggers, and loaders handling the 8E formulation in Table 1 are based on the Knarr, 1980 study. The workday in Maddy *et al*., 1982 study in California was two to four hours of Ordram application and the remainder of the day fertilizer and seed applications. This is a common practice for most rice herbicide applications in California. The workdays in Knarr, 1980 study in Arkansas were 1.5

to four hours during the 10G formulation and 1.5 to nine hours during the 8E formulation. The exposure estimates in Table 1 were normalized for a four-hour workday.

In the 1990 worker exposure study conducted by Chester (1991) in Arkansas, Ordram® 15G was applied by air. Both 50-lb and 1500-lb bulk bags were used. The exposure was monitored both by dosimetery and biomonitoring. In the biomonitoring portion, workers' absorbed dosages were estimated based on the amount of molinate mercapturate found in the urine samples. Later, further investigation of the pharmacokinetics of molinate in humans following a single oral dose determined that 4-hydroxy molinate was the major metabolite of molinate in urine. The urine samples of loaders were then analyzed for 4-hydroxy molinate and the results were reported (Chester *et al.*, 1992). The averages (arithmetic mean $\pm$ standard deviation) estimated ADD based on 4-hydroxy molinate for loaders of 50-lb bags and loaders of 1500-lb bags were 788 $\pm$ 428 (geometric mean = 711) and 491 $\pm$ 210 (geometric mean = 450) ug/kg/day, respectively. There were 12 replicates for 50-lb bags and nine replicates for 1500-lb bags. A t-test showed that there is a significant difference (α=0.05) between the two means, demonstrating a modest advantage in using bulk bags in exposure reduction.

In 1991, a study was conducted in Arkansas in which the loading of Ordram® 10G into airplane hoppers was simulated, using two loading techniques (ICI, 1991). Either 1500-lb or 350-lb bags were loaded. The first technique (trans-loading) involved loading the bulk bags into a hopper truck and then into the airplane simulator (bin). A fan was positioned at the loading site to provide an airflow simulating an airplane. Bags were lifted using a forklift. One loader opened the bag and guided the material into the truck hopper and then emptied the truck hopper into the airplane simulator. The other loader rode with the hopper truck. The second technique (direct-loading) involved direct loading into the airplane simulator. One loader remained inside the cab of the truck which was positioned as the lifting device while the other one emptied the bag into the plane simulator. The two loaders traded places so that each drove and loaded the same number of bags.

The exposure of workers to molinate was estimated by analyzing workers' full 24-hour urine samples for 4-hydroxy molinate. Urine samples were collected for 24 hours prior to loading, for the day of loading, and for two days after loading. No 4-hydroxy molinate was detected in samples collected prior to the day of loading. Results were corrected for molecular weight difference, the metabolite (4-hydroxy molinate) representing 39 percent of the dose in urine (Batten *et al*., 1992 in the metabolism section), and actual body weight. Workers wore goggles, rubber gloves, hat, long-sleeved shirt, long pants, and shoes. The exposure for each worker was expressed as a three-day average. Estimates of ADD for loaders (n=10) of the trans-loading technique and loaders (n=10) of the direct-loading technique were 40.5 $\pm$ 28.9 (geometric mean = 30.9) and 15.1 $\pm$ 7.4 (geometric mean = 13.2) ug/kg/day, respectively.

Workers' exposure to molinate was monitored in Sacramento Valley during actual loading of Ordram® 10G for aerial application (ICI, 1992a). Two loading techniques as described in the previous the previous ICI (1991) study were used. The direct loading involved bulk containers (1500 lb bags) and the trans-loading involved both the bulk containers and 50-lb bags. A total of 20 workers were monitored. Each worker was monitored for three days of exposure and one day of pre-exposure as a baseline. Attempts were made to assure the workers were not exposed to molinate the day before the exposure day started (baseline day), but the study report indicates that workers did handle molinate on "baseline day". Workers were divided into four job classifications as follows: 1) Direct-loading drivers (n = 2) who remained in a closed cab during loading; 2) Trans-loading drivers (n =5), who would leave the closed cab to assist the loader, after hoisting the bag; 3) Direct-loading loaders (n = 3), who were involved only in emptying the bag into the airplane hopper; and 4) Trans-loading loaders (n = 10), who were involved in emptying the bags into a bucket and then into the airplane hopper.

Urine samples were taken starting on the morning of the pre-exposure day and finishing with the first void of the day after the last monitoring day. Personal air sampling pumps equipped with XAD-2 solid sorbent resin tubes were used to take air samples from workers' breathing zones. Urine samples were analyzed for 4-hydroxy molinate and the results were corrected for the metabolite representing 39 percent of the dose and molecular weight difference between the metabolite and molinate. The majority of workers did not wear clean chemical-resistant suits every day. Some workers wore the same suit during the entire monitoring period. Generally all workers wore the full face respirator during loading but there was a question of whether the filters were changed at all. Use permit deviations such as loading both bulk (1500 lb) and small (50 lb) bags, and not wearing respirator or gloves during loading were considered significant. Table 2 shows molinate ADDs and molinate residues in the breathing zones for different job classifications when work was done in compliance with permit conditions. Air monitoring data suggest that most of the exposure occurred via dermal route.

Table 2
Workers' Estimated ADDs of Molinate
During Actual Loading of Ordram® 10G from 1500-lb Bags

Job Classification (n)	ADD* ug/kg/day	Air residues* ug/m^3	Ordram Handled lb/person/day
Direct-loading:			
driver (6)	1.26 ± 1.82	2.09 ± 1.83	
loader (9)	3.31 ± 2.61	6.78 ± 4.63	2500
Trans-loading:			
driver (11)	2.78 ± 1.60	7.19 ± 3.59	
loader (23)	10.31 ± 2.54	27.41 ± 4.41	6220

n - Number of replicates
* - Geometric mean ± geometric standard deviation (log-normally distributed).
Clothing consisting of work clothing, full-body chemical resistant suit, hat, chemical
resistant gloves, full-face respirator, and chemical resistant foot coverings.

In 1992, ICI Americas conducted a study to measure the exposure of workers to a new formulation (montmorillonite) of molinate during simulated direct-loading and trans-loading of 1250-lb bulk bags (ICI, 1992b). The trans-loading operation was monitored using a hopper truck equipped with and without

Table 3
Workers' ADDs of MolinateDuring Simulated
Loading of Ordram® 10G from 1250-lb Bags

Loading Method (n)	ADD* (ug/kg/day)
Direct-loading (10)	3.0 ± 2.25
Trans-loading (shroud) (10)	5.3 ± 2.91
Trans-loading (no shroud) (10)	6.6 ± 2.35

n- Number of replicates
* - Geometric mean ± geometric standard deviation (log-normally distributed).

a metal shroud. There were ten replicates for each situation monitored. Urine samples were taken the day prior to and the day of loading for each worker. All workers wore work clothing, chemical resistant suit, chemical resistant gloves, hat, full-face respirator, and shoe coverings. The study conditions and loading operation were similar to the ICI (1991) study. Approximately 29,000 lb of Ordram 10G were handled by the two loaders a day. The results (Table 3) were corrected for 39 percent 4-hydroxy molinate in urine, and the molecular weight difference.

Zeneca, Inc. monitored the exposure of workers (44 replicates) to the new formulation of molinate (montmorillonite formulation) during actual direct-loading and trans-loading of Ordram® 10G in rice-growing areas of Sacramento Valley (Zeneca, 1993a). Bulk bags (1280 lb) of Ordram® 10G were used. Direct loading accounted for 78 percent of all the loading recorded. Direct loading has been the preferred method because it is faster and the bag limit was higher resulting in reduced labor cost. Approximately four to five percent of the total molinate applied in California during 1993 was monitored during the course of this study.

Workers were monitored for a period of four days. A baseline day or pre-exposure day (when commercial practices of applicators made it possible) was followed by three additional days with at least one day in which a minimum of four bags of Ordram® 10-G were loaded. Workers wore all the personal protective equipment required under molinate permit conditions, but the collection, moving, and recycling of empty bags were performed without the use of mitigation. Workers wore either Tyvek or carbon suits (activated spherical carbon impregnated suits). The study was a crossover design such that each worker first wore one suit and then the other suit for three workdays each. Workers were classified according to their activities (loading technique) and protective suits (type of suit) as shown in Table 4.

With a few exceptions that should not affect the integrity of the study, the study was conducted in compliance with EPA's Good Laboratory Practice (GLP) requirements. These exceptions included the analysis of the test substance by a non-GLP laboratory, the loss of labels from some bulk bags of test substance during transit resulting in the loss of batch numbers for those bags, and weather data obtained with instrumentation and/or calibration procedures not in accordance with full GLP. A 24-hour urine sample was taken from each worker starting with the first void of the day to the first void of the following day. Urine samples were collected from all participants over the entire monitoring period. Control and 4-hydroxy molinate-spiked urine samples were prepared and the spiked samples were placed under the same field conditions as those of participants. Mean field recovery was 104 percent. The results were not corrected for the field recoveries, slightly overestimating the exposure. All urine samples were frozen

Table 4
Workers' Estimated ADDs of Molinate During Actual Loading
of a New Formulation (montmorillonite) of Ordram® 10G from 1280-lb Bags

Work Task (n)	Loading Technique	Type of Suit Worn	ADD* (ug/kg/day)	Amount Loaded (1b./day)	Absorbed Dose (ug/kg/1000 lb.)
loaders:					
10	direct loading	Tyvek	5.84 ± 2.70	9323	0.63
9	direct loading	Carbon	2.63 ± 2.54	6424	0.41
9	direct + trans	Tyvek	6.10 ± 2.02	8208	0.74
6	direct + trans	Carbon	10.58 ± 1.70	10880	0.97
Drivers:					
5	None	None	0.76 ± 2.31		
5	None	Carbon	0.56 ± 2.20		

* - Geometric mean and geometric standard deviation (log-normally distributed).
(n) - Number of workers.

following collection by the study personnel. Urine samples were analyzed for 4-hydroxy molinate. The results (Table 4) were corrected for 39 percent recovery of molinate in urine as 4-hydroxy molinate and the molecular weight difference. The exposure for each worker was expressed as a three-day average.

The estimate of exposures for loaders wearing Tyvek or carbon suits during direct loading or direct plus trans-loading are shown in Table 4. For two out of three work tasks monitored (direct loading and drivers), the estimated exposure values for workers wearing carbon suits are lower than those wearing Tyvek or no protective clothing. It is not clear why the work task that requires handling the Ordram® twice (trans-loading) resulted in higher exposure for persons wearing carbon suits than Tyvek.

The maximum number of 1,200-lb. bags which could be loaded directly by an individual in a given day would be 14 (16,800 lb. of the 10G formulation), based on physical limitations (Ross, 1994). An individual doing direct loading for the season would be limited to 226,800 lb. (189 bags) based on the seasonal margin of safety (Cochran, 1994). The weight limit for an individual doing a combination of direct and trans-loading for the season would be 135,000 lb., also based on the seasonal margin of safety (Cochran, 1994). The seasonal average daily dosages (SADDs) in Table 5 were calculated based on the estimated absorbed doses/1000 lb. in Table 4 and the above bag limits.

Table 5
Workers' Estimated ADD, SADD, and AADD During Loading
of a New Formulation (montmorillonite) of Ordram® 10G from Bulk Bags

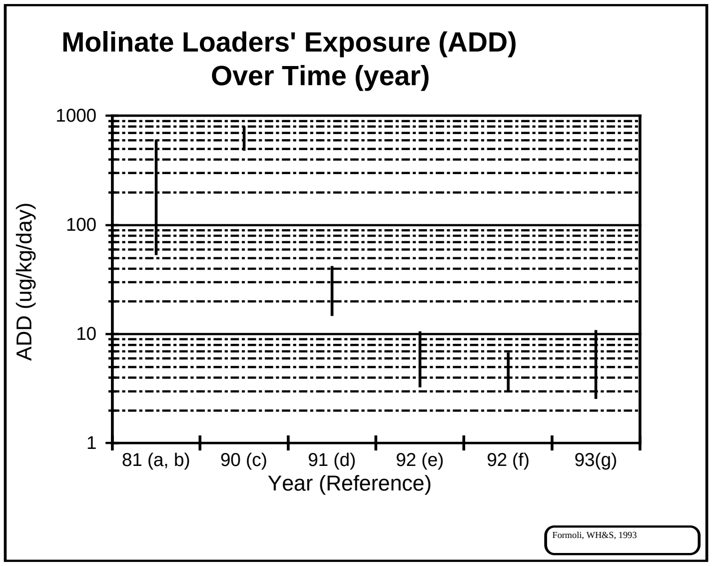
Work Task	Type of Suit Worn	Absorbed Dose (ug/kg/1000 lb.)	ADD* (ug/kg/day)	SADD** (ug/kg/day)	AADD*** (ug/kg/day)
direct loader	Tyvek	0.63	10.58	4.10	0.39
direct loader	Carbon	0.41	6.89	2.66	0.25
direct + trans	Tyvek	0.74	3.7	2.85	0.27
direct + trans	Carbon	0.97	4.85	3.74	0.36
driver	None		0.76		
driver	Carbon		0.56		

* - ADD based on daily direct loading of 16,800 lb. or direct plus trans-loading of 5,000 lb. of Ordram 10G.
** - SADD based on direct loading of 226,800 lb. or direct plus trans-loading of 135,000 lb. during approximately 27 days of handling period in a 35-day season (Zeneca, 1993b).
*** - Annual average daily dosage (AADD) based on 27 days of handling molinate in a 365-day year.

While inhalation exposure is significant, dermal exposure appears to be the major route of exposure for workers handling molinate 10G formulation (see Tables 1 & 2). The earlier worker exposure studies showed that loaders of Ordram® 10G have the greatest potential for exposure to molinate compared to the pilots and flaggers. Based on the earlier studies (Maddy *et al*., 1982; Knarr, 1980), the ADD for pilots was conservatively estimated at 3.5 ug/kg/workday (Table 1). In Maddy et al., 1982 study, most of the dermal exposure samples for pilots had no detectable residues and these samples were assumed to contain residues at half the MDL. In addition, the work practices, engineering controls, and personal PPE have improved dramatically since these studies were conducted. The use of bulk bags, direct loading, and improved formulation (montmorillonite) may have reduced the exposure to pilots from the levels estimated based on earlier studies. The ADD of 10.5 ug/kg/day for flaggers was also estimated based on Maddy *et al*., 1982 and Knarr, 1980 studies. The current (1994) molinate use permit requires flaggers to stay in an enclosed vehicle during application or wear coveralls (in addition to work clothing), goggles, head covering, chemical resistant gloves, and a half-face respirator. These exposure mitigation alternatives should provide 90 percent dermal and inhalation exposure protection (Thongsinthusak *et al*., 1991) to flaggers and reduce the estimated exposure in Table 1 to 1.1 ug/kg/workday.

The more recent studies focused mainly on monitoring the exposure of workers involved in loading Ordram® 10G for aerial applications. These studies show a gradual decline in molinate exposure to loaders as more reliable monitoring techniques, improved formulation, and additional exposure mitigation measures were systematically implemented over the years. Figure 1 shows the estimated range of exposure to loaders.

Figure 1



a) Knarr, (1980)
b) Maddy, et al., 1982
c) Chester,et al., 1992.
d) ICI, 1991
e) ICI, 1992a
f) ICI, 1992b
g) Zeneca, 1993a

Protective Clothing and Engineering Controls:

a, b) Long- sleeved shirts, long pants, chemical resistant gloves, loading of 50-lb bags of Ordram 10G.

c) Long- sleeved shirts, long pants, chemical resistant gloves, goggles, loading 50-lb and 1500-lb bags of Ordram 15G.

d) Long- sleeved shirts, long pants, chemical resistant gloves, goggles, hat, leather shoes, direct loading and trans-loading of 350-lb and 1500-lb bags of Ordram 10G.

e) Work clothing, chemical resistant suit, chemical resistant gloves, full-face respirator, hat, shoe coverings, direct-loading and trans-loading of 1500-lb bags of Ordram 10G.

f) Work clothing, chemical resistant suit, chemical resistant gloves, full-face respirator, hat, shoe coverings, direct-loading and trans-loading (with and without shroud) of 1250-lb bags of a new formulation (montmorillonite-based) of Ordram 10G.

g) Work clothing, chemical resistant suit (Tyvek or carbon-impregnated), chemical resistant gloves, full-face respirator, hat, shoe coverings, direct-loading or direct plus trans-loading of 1280-lb bags of Ordram 10G (montmorillonite formulation).

The quantity of the emulsifiable concentrate formulation of molinate (Ordram® 8E) used in California is limited compared to that of the granular formulation. The use of Ordram 8E by air is prohibited in California. It can be used by ground equipment as a preplant soil incorporation. There are no studies that monitored molinate exposure to workers involved in ground application of Ordram 8E. The pesticide handlers exposure database (PHED), a software system that was developed by Versar Inc., was used as surrogate to obtain an estimate of exposure for mixer/loader/applicators (M/L/A) of Ordram 8E. There were 20 records for the M/L/A file with emulsifiable formulation and ground boom application subsets. There were no (zero) records for the soil incorporation method of application. The estimate of dermal exposure for a M/L/A wearing long-sleeved shirt, long pants, and gloves was 27.1 ug/lb a.i. sprayed (see attachment II). Molinate use permit conditions require workers handling the liquid formulation of molinate to wear chemical resistant coveralls or chemical resistant full-body protective clothing, a full-face respirator, chemical resistant foot coverings, and a tightly woven head covering in addition to a long-sleeved shirt, long pants, and chemical resistant gloves. The additional PPE should provide 95 percent dermal protection to the covered areas (Thongsinthusak *et al*., 1991) and reduce the PHED estimated dermal exposure to 2.3 ug/lb a.i. sprayed. Based on an application rate of 3 lb a.i./acre, treatment of 40 acres in a workday, and dermal absorption of 53 percent, the ADD for a ground M/L/A weighing 75.9 kg will be 1.9 ug/kg/day.

Because of the fairly high vapor pressure of molinate, it is not appropriate to use the estimate of inhalation exposure from the PHED. Air samples collected from the breathing zone of the ground crews during aerial applications of Ordram 8E showed an average molinate residues of 54 $\pm$ 46 ug/m^3 (Knarr, 1980). With a full-face respirator providing 98 percent protection for inhalation exposure (Thongsinthusak, *et al.*, 1991), respiratory exposure of a ground M/L/A of Ordram 8E to molinate will be insignificant, assuming that the air in their breathing zone is in the same range as observed in the Knarr, 1980 study.

Potential exposure to workers entering treated fields following molinate application is mainly respiratory since no dermal contact is expected. Air samples taken from four feet above the water surface of rice fields showed 48 ug/m^3 molinate immediately after application (Ross and Sava, 1986). Molinate concentration declined to 8.3 ug/m^3 three days after the application. The three-day average concentration was 21.9 ug/m^3. The estimate of ADD for a worker spending one hour a day in a treated rice field is 0.12 ug/kg/day, using the average molinate concentration, male inhalation rate of 0.84 m^3/hour, a body weight of 75.9 kg (Thongsinthusak, 1993), and inhalation uptake of 50 percent (Raabe, 1988).

In the 1992 worker exposure study (ICI, 1992b), the exposure to loaders using transloading equipment with and without a cover were monitored. The mean exposure to workers using a hopper truck equipped with a metal cover was lower than the mean exposure to those using a hopper truck without a cover (see Table 3). However, a t-test at $\alpha = 0.05$ indicated that the exposure difference between the two types of equipment was not significant. In addition, site air monitoring data were collected by the Department during transloading operation using hoppers equipped with and without a cover (Schneider, 1994). Air samples were taken from near the middle of the bucket and also from near the edge of the bucket. A sampling train consisting of a glass fiber filter cassette followed by a solid sorbent resin tube was used. Arthimetic mean molinate levels were 0.967 (n=4, SD=0.74), 0.439 (n=5, SD=0.663), and 0.316 (n=6, SD=0.232) ug/L for the hopper with pvc funnel and cover, the hopper with flat cover, and for the hopper without a cover, respectively. Results of ANOVA (p=0.21) indicated no significant difference between the three groups.

The worker safety permit conditions for 1994 (section II-A) require the use of a transloader cover when loading granular molinate to the transfer equipment. However, some aerial applicators of molinate were experiencing problems when loading two bags into a transloader equipped with a cover. The cover would impede the process and would create a barrier to the material, creating the potential for greater exposure. Therefore, the Department allowed the use of trans-loading equipment without a transloader cover (Andrews, 1994).

Non-Occupational Exposure

Members of the general population with potential exposure to molinate include those who regularly eat rice and those served by the water utilities using the Sacramento River as the source of drinking water. The Sacramento River receives water drained from the Sacramento Valley rice fields treated with molinate. Potential routes of exposure to molinate in the drinking water supply include ingestion as well as inhalation and dermal contact from general household uses. Exposure to molinate in the ambient air is also a concern for the general public residing in communities in the proximate vicinity where molinate is applied by aerial spraying.

1. Water Supplies (Sacramento/West Sacramento)

a. Oral Route

Table 6 shows the peak concentrations of molinate detected at various monitoring sites from 1986 to 1990 (O'Brian, 1989; CDFA, 1986, 1987, 1989, 1991b). The peak concentrations at all sites were found around mid-May through mid-June of the year. Concentrations detected at the Colusa Basin Drains ranged from 16 to 59 ppb during the peak period of 1990 with an average concentration of about 35 ppb. The Sacramento

River water had concentrations ranging from 2 to 9 ppb and an average concentration of 4 ppb during the same period.

Table 6
Water Concentrations of Molinate Detected at Various
Monitoring Locations in 1986 to 1990*

Locations		Concentration (ppb)			
	1986	1987	1988	1989	1990
CBD1 Maximum	77	43	67	51	51
Average**	52	35	47	37	35
	(7.4)	(2.8)	(5.1)	(3.1)	(5.0)
CDB5 Maximum	88	53	89	60	59
Average**	67	37	55	40	34
	(9.4)	(3.3)	(7.5)	(3.6)	(6.3)
SR1 Maximum	11	8	8	6	9
Average**	6	5	6	4	4
	(0.7)	(0.8)	(0.5)	(0.5)	(0.9)
SRR Maximum	14	6	5	5	7
Average**	5	3	3	2	4
	(0.6)	(0.4)	(0.2)	(0.3)	(0.3)

* Samples taken by either the City of Sacramento or the California Department of Fish and Game.

** Data represent the arithmetic mean concentrations detected during the peak period from mid-May to mid-June. Numbers in the parenthesis are standard errors. Only concentrations $\geq$ 20 ppb for CBD1 and CBD5 and $\geq$ 2 ppb for SR1 and SRR are included in the calculations unless they are within the peak period.

CBD1: Colusa Basin Drain at Roads 109 and 99E near Knight's Landing in Yolo County.

CBD5: Colusa Basin Drain at Highway 20 in Colusa County.

SR1 : Sacramento River at Village Marina in Sacramento County considered to be representative of the intake for the West Sacramento.

SRR : Sacramento River at the intake to the City of Sacramento water treatment facility.

Molinate is oxidized to its sulfoxides by the chlorination process employed in the water treatment facilities (Ross, 1983). Analyses performed by the City of Sacramento from 1983 to 1986 indicated that molinate was not detected in the tap water (CDFA, 1984; Myers, 1983-89). On the other hand, molinate sulfoxide was found in the finished tap water at a level comparable to the level of the parent molinate observed in the pretreated Sacramento River raw water. DPR concurred with the opinion of the CDHS that measurements of the molinate concentration in Sacramento River water intake for the water treatment facilities could be used as a surrogate to evaluate potential human exposure to molinate and its by-products in drinking water supplies (Berteau, 1984).

California Department of Health Services (CDHS) set a maximum concentration level (MCL) of 20 *u*g/L for molinate in drinking water (CDHS, 1989). Based on the 1990 data, molinate concentrations of 2 to 9 ppb (*u*g/L) detected in the Sacramento River water were below the MCL of 20 *u*g/L. The potential daily exposure dosages of molinate and its by-products from ingesting water from Sacramento River are presented in Table 7. Young children residing in West Sacramento potentially ingested an average of 0.43 *u*g/kg/day to a maximum of 0.89 *u*g/kg/day during mid-May to mid-June. The potential average daily dosage and maximum daily dosage for adults was 0.12 *u*g/kg and 0.25 *u*g/kg, respectively. The potential daily dosage of molinate and its by-products from drinking water for residents in the City of Sacramento was about 80 percent of that observed for residents in West Sacramento.

Table 7
Potential daily exposure to molinate from drinking water*

Sources	Exposure Dosage (*u*g/kg/day) Adult Average	Adult Maximum	Child Average	Child Maximum
SR1	0.12	0.25	0.43	0.89
SRR	0.10	0.19	0.35	0.65

* Assumes 70 kg body weight and daily water consumption of 2 liters for adults. Assumes 10 kg body weight and daily water consumption of 1 liter for the child.
SR1 Sacramento River at Village Marina in Sacramento County considered to be representative of the intake for West Sacramento.
SRR Sacramento River at the intake to the City of Sacramento water tr

Molinate concentrations in the Sacramento River peaked from mid-May to mid-June, coinciding with the seasonal application of the herbicide in rice fields and the subsequent drainage of the contaminated water into the Sacramento River after a holding period of up to 19 days. The duration of exposure to detectable concentrations of molinate in drinking water is approximately one month per year. The arithmetic average water concentration during the peak period is used to estimate the potential exposure level.

Even though the use-season for molinate is limited to a 6-week period, data suggest the neurotoxic effects of molinate may not be reversible (Cochran, 1994). Consequently, the potential annual exposure to molinate was also calculated. As detectable levels of molinate have been measured in the river water for approximately 30 days each year, the annual exposure would equal the seasonal exposure multiplied by 30 days/365 days per year. Thus, the annual exposure from drinking water would range from 0.01 *u*g/kg/day for adults to 0.04 *u*g/kg/day for children in West Sacramento.

The combined potential exposure dosage from daily ingestion of rice and water from the Sacramento River ranges from 0.13 *u*g/kg/day for the adult population to 0.46 *u*g/kg/day for non-nursing infants less than one year old, with major contribution being from the water (Table 8). The combined potential exposure for ingestion of rice and water ranges from 0.04 *u*g/kg/day for adults to 0.07 *u*g/kg/day for children.

Table 8
Combined potential exposure of West Sacramento residents to molinate
from drinking water and diet (rice).

Population	Exposure Dosage (*u*g/kg/day) Rice	Water*	Combined
Adults	0.005	0.12	0.13
Non-Hispanics Other Than Black and White	0.029	0.12	0.15
Nursing Infants (<1 year old)	0.007	0.43	0.44
Non-Nursing Infants (<1 year old)	0.029	0.43	0.46

* Data is taken from Table 7, the Average Daily Dosage from SR1, Sacramento River water intake for West Sacramento.

b. Inhalation Route

Molinate is very volatile, and evaporation is expected to be the major route of dissipation from water. In general, volatility also increases with the increase in temperature when water is used for showering, laundry, and washing purposes. It is suggested that the contribution from inhalation of volatile organic compounds, such as tetrachloroethene and trichloroethene, from domestic uses of the water supply could

Table 9
Comparison of Henry's Law Constant at 20°C

Compounds	Henry's Law Constant
Molinate	0.000065
Tetrachloroethene	0.847
Trichloroethene	0.393

$$\text{Henry's Law Constant H} = \frac{\text{Concentration in Air } (u\text{g/L})}{\text{Concentration in Water } (u\text{g/L})} = \frac{16.04\ P*M}{T*S}$$

Where: P is the equilibrium vapor pressure in torr.
M is the gram molecular weight per mole.
T is the temperature in °K. °K = 273 + °C.
S is the solubility in water in mg/L.

be as much as that from the ingestion of two liters of water (Andelman, 1985). A comparison of the calculated Henry's Law Constant (Table 9) shows that the volatility of molinate is about 0.007 to 0.015 percent of that for tetrachloroethene and trichloroethene. Therefore, the potential exposure to molinate via inhalation from household uses of the water supply is expected to be negligible.

c. Dermal Route

Dermal contact with contaminated water while swimming or bathing is a potential route of exposure to molinate. However, as environmental factors (water temperature and flow volume) limit swimming in the Sacramento River and adjacent waterways during May, and no molinate was measured in domestic waters supplies, it is believed that the dermal route is insignificant compared to the oral and inhalation routes.

2. <u>Ambient Air</u> (Maxwell and Williams)

a. Inhalation

In 1986, the ambient air concentrations of molinate were measured on the rooftops of the public buildings in four Sacramento Valley towns (Seiber *et al*., 1989). Sampling was carried out for four 24 hour intervals (Monday a.m. through Friday a.m.) for four weeks during the period selected to represent the highest uses of molinate. The measurement of ambient air concentration did not discriminate between fine particulate aerosol and the vapor phase of molinate (Mischke, 1989). The maximum concentration and the highest arithmetic average concentration were detected at Maxwell at 1.7 $u\text{g/m}^3$ and 0.65 $u\text{g/m}^3$, respectively. After adjusting for the collection efficiency of 67 percent, the arithmetic average ambient air concentration of molinate encountered by residents of Maxwell was 0.28 $u\text{g/m}^3$.

The arithmetic average ambient air concentration of molinate in 1992 at Maxwell according to measurements taken by the California Air Resources Board was 0.72 $u\text{g/m}^3$ (range = 0.4 to 1.17 $u\text{g/m}^3$) and at Williams it was 0.39 $u\text{g/m}^3$ (range = 0.16 to 0.50 $u\text{g/m}^3$) (EMPM, 1992).

Using the standard default value for human inhalation of 0.29 m^3/kg/day for adults and 0.6 m^3/kg/day for infants (Anderson *et al*., 1983), and assuming a 50 percent retention and 100 percent absorption (Raabe, 1986, 1988), the estimated seasonal dosage for an individual in Maxwell in 1986 was:

Adults- (0.28 *u*g/m^3)x(0.29 m^3/kg/day)/2 = 0.04 *u*g/kg/day

Infants- (0.28 *u*g/m^3)x(0.6 m^3/kg/day)/2 = 0.09 *u*g/kg/day

The estimated seasonal dosage for an individual in Maxwell in 1992 was:

Adults- (0.72 *u*g/m^3)x(0.29 m^3/kg/day)/2 = 0.10 *u*g/kg/day

Infants- (0.72 *u*g/m^3)x(0.6 m^3/kg/day)/2 = 0.22 *u*g/kg/day

The estimated seasonal dosage for an individual in Williams in 1992 was:

Adults- (0.39 *u*g/m^3)x(0.29 m^3/kg/day)/2 = 0.06 *u*g/kg/day

Infants- (0.39 *u*g/m^3)x(0.6 m^3/kg/day)/2 = 0.12 *u*g/kg/day

Potential annual exposures may be estimated by amortizing the seasonal dosage (which occurs during a 35 day period) over the entire year (365 days). Thus, the arithmetic average annual daily dosage would be equivalent to the seasonal dosage multiplied by 35/365:

Maxwell	1986	1992
Adults	0.004 *u*g/kg/day	0.01 *u*g/kg/day
Infants	0.009 *u*g/kg/day	0.021 *u*g/kg/day
Williams		
Adults	not measured	0.006 *u*g/kg/day
Infants	not measured	0.012 *u*g/kg/day

A theoretical worst case scenario can be derived from the supposition that a family could live in a home adjacent to a treated rice field. Rice fields are only treated once during the rice growing season, so the exposure would follow the pattern described by Ross and Sava (1986). They reported that the highest measured air concentration of molinate, 48 cm above the surface of a treated rice paddy, was 48 *u*g/m^3 on the day of application. However, the air concentrations dropped precipitously with time, theoretically reaching non-detectable levels in a week. The 5 day arithmetic average was estimated to be 18.7 *u*g/m^3. Theoretically, individuals living in a home next to the rice paddy would receive the following short-term daily dosages through the inhalation route:

Adults- (18.7 *u*g/m^3)x(0.29 m^3/kg/day)/2 = 2.71 *u*g/kg/day
Infants- (18.7 *u*g/m^3)x(0.6 m^3/kg/day)/2 = 5.61 *u*g/kg/day

As a rice paddy is treated only once during the year with molinate, there would not be a seasonal, or annual exposure to consider.

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Attachment I

MOLINATE (ORDRAM) WORKER SAFETY PERMIT CONDITIONS
(1994)

The Worker Safety Permit conditions for Molinate (Ordram 8E and 10G) have changed. Please read these conditions carefully for changes which will affect application of this material.

WORKER PROTECTION

I. Training

A. All persons, prior to handling molinate, must be trained and maintain proof that they attended or were trained by an attendee of a 1994 worker protection training program approved by the Department of Pesticide Regulation (DPR).

B. Employers shall maintain records of the date and name of each person who received training. Records shall be made available for inspection upon request by the county agricultural commissioner or the Director.*

II. Engineering Controls

A. A transloader cover must be used when transferring granular molinate from the bag to transfer equipment. This cover must fit the opening and reduce escaping dust.

B. Liquid molinate (Ordram 8E) shall not be applied by air.

C. If an enclosed cab is used which meets criteria for Type 2 enclosed cabs, ground applicators shall wear cloth coveralls, or long-sleeved shirt and long-legged trousers. However, the applicator shall have available a full-face respirator, gloves, and foot coverings in the cab. This equipment shall be worn when exiting the cab and coming in contact with contaminated soil or equipment.

III. General Requirements

The employer shall provide and require employees to wear all necessary protective clothing as specified, and provide for cleaning, repair, and replacement when necessary. All protective clothing and equipment are the property of the employer.

A. Aerial Application Handling Requirements (Granular Formulation)

1. Bag Handling Requirements

a. No person shall load more than the equivalent of 190 bags of Ordram 10G per season (228,000 pounds total).

b. Ordram 10G shall be loaded only in the following manner:

(1) Directly from the bulk bag into the application vehicle hopper (direct loading); or

(2) Directly from the bulk bag into a loading cone and then to the application vehicle hopper (transloading).

c. The employer shall maintain a record of persons loading Ordram 10G and make these records available for inspection by the county agricultural commissioner or the Director upon request. Records shall be kept as follows:

(1) Name of person.

(2) The date and total pounds of Ordram 10G loaded per day.

2. Loaders or any persons having contact with full, or handling partial, or empty Ordram 10G bags shall wear the following personal protective clothing and equipment:

a. A charcoal cloth suit (long-sleeved and long-legged) as the underlayer.

b. Either a cloth coverall or long-sleeved shirt and long-legged trousers as the outer layer [equivalent to work clothing as defined in California Code of Regulations (CCR) Section 6000.4(s)].

c. A tightly woven head covering.

d. Chemical resistant foot coverings.

e. Chemical resistant gloves.

f. NIOSH or MSHA approved full-faced respirators having both dust and organic vapor pesticide cartridges.

3. Pilots shall wear the following personal protective clothing and equipment.

a. Cloth coveralls or long-sleeved shirt and longlegged trousers [equivalent to work clothing as described in CCR Section 6000.4(s)].

b. Pilots involved in loading or equivalent activities (load leveling, handling the bucket sock) where they may come in contact with Ordram 10G shall wear the same protective clothing and equipment as required for loaders in III, A, 2.

4. Flaggers shall wear the following personal protective clothing and equipment:

a. Two layers of any of the following:

(1) Cloth coveralls or long-sleeved shirt and long-legged trousers [equivalent to work clothing described in CCR Section 6000.4(s)].

(2) Disposable coveralls (long-sleeved and long-legged) made of synthetic materials capable of excluding particles 45 microns or larger in diameter. Examples of these are Tyvek Q, Kleen Guard, Polypropylene, or other brands of coveralls approved by the Worker Health and Safety Branch, DPR.

b. Protective eyewear (safety glasses)

c. NIOSH or MSHA approved half-face respirator having organic vapor pesticide cartridges.

d. Tightly woven head covering.

e. Chemical resistant gloves.

f. If an enclosed vehicle is used while flagging, flaggers shall wear cloth coveralls or long-sleeved shirt and long-legged trousers. However, the flagger shall have available a respirator, protective eye wear, gloves, and head covering in the vehicle. This equipment shall be worn when exiting the vehicle during the application to perform flagging activities.

B. Ground Application Requirements

1. Granular Formulation Requirements

a. Ground applicators shall wear the following personal protective clothing and equipment:

(1) Two layers of any of the following:

(a) Cloth coveralls or long-sleeved shirt and long-legged trousers [equivalent to work clothing defined in CCR Section 6000.4(s)].

(b) Disposable coveralls (long-sleeved and long-legged) made of synthetic materials capable of excluding particles 45 microns or larger in diameter. Examples of these are Tyvek Q**, Kleen Guard**, Polypropylene**, or other brands of coveralls approved by the Worker Health and Safety Branch, DPR.

(2) NIOSH or MSHA approved full-faced respirator having both dust and organic vapor pesticide cartridges. A respirator is not required for applicators using ground equipment that injects or incorporates molinate into soil.

(3) Chemical resistant gloves.

(4) Chemical resistant foot coverings.

(5) If an enclosed cab is used which meets criteria for Type 2 enclosed cabs, ground applicators shall wear cloth coveralls or long-sleeved shirt and long-legged trousers. However, the applicator shall have available a full-face respirator, gloves, and foot coverings in the cab. This equipment shall be worn when existing the cab and coming in contact with contaminated soil or equipment.

2. Liquid Formulation Requirements

a. All handlers (mixers, loaders, and applicators) shall wear the following protective clothing and equipment:

(1) Two layers of the following:

(a) Cloth coveralls or long-sleeved shirt and long-legged trousers [equivalent to work clothing described in CCR Section 6000.4(s)], and

(b) Chemical resistant coveralls (long-sleeved and long-legged) or equivalent to 6738(d)(1): ...chemical resistant full body protective clothing that covers the torso, head, arms, hands, legs, feet. Examples of these are Tyvek QC**, Tyvek laminated with Saranex**, Polypropylene laminated with polyethylene**, Encase II** or other brands of coveralls approved by the Worker Health and Safety Branch, DPR.

(2) NIOSH or MSHA approved full-faced respirator having organic vapor pesticide cartridges. Respirators are not required for applicators using ground equipment that injects or incorporates molinate into the soil or when using vehicle-mounted spray nozzles which are both located below the applicator and are directed downward.

(3) Chemical resistant gloves.

(4) Chemical resistant foot coverings.

(5) A tightly woven head covering.

b. Persons using a closed system that meets the Director's criteria are not required to wear chemical resistant coveralls and full-faced respirator. However, a chemical resistant apron shall be worn.

c. If an enclosed cab is used which meets criteria for Type 2 enclosed cabs, ground applicators shall wear cloth coveralls or long-sleeved shirt and long-legged trousers. However, the applicator shall have available a full-face respirator, gloves, and foot coverings in the cab. This equipment shall be worn when exiting the cab and coming in contact with contaminated soil or equipment.

CCR Section 6000.4(s)

"Work Clothing" means a long-sleeved shirt and long-legged trousers or a coverall-type garment, all of closely woven fabric or equivalent covering the body, including arms and legs. The clothing need not cover the head, hands or feet.

Type 2 Enclosed Cab Criteria

These cabs must provide a nonporous physical barrier totally surrounding the worker in the cab that prevents contact with dust or spray mist. A type 2 enclosed cab may have air intakes, heating and air conditioning.

* The term Director means employees of DPR or agents of the Director.
** Use of brand names does not imply endorsement by DPR.

Attachment II

Summary Statistics Developed in PEHD
for a Ground Mixer/loader/applicator of Ordram 8E

SUMMARY STATISTICS FOR CALCULATED DERMAL EXPOSURES

SCENARIO: Long pants, long sleeves, gloves

PATCH LOCATION	DISTRIB. TYPE	MICROGRAMS PER LB AI SPRAYED Median	Mean	Coef of Var	Geo. Mean	Obs.
HEAD (ALL)	Lognormal	24.96	43.394	124.5027	19.2875	20
NECK.FRONT	Lognormal	1.155	8.4143	270.133	1.4842	20
NECK.BACK	Lognormal	3.344	2.7456	102.7462	.8417	15
UPPER ARMS	Lognormal	.582	1.552	108.2539	1.0576	3
CHEST	Lognormal	.71	1.42	86.6056	1.127	3
BACK	Lognormal	.71	1.42	86.6056	1.127	3
FOREARMS						0
THIGHS	Other	.764	.764	0	.764	3
LOWER LEGS	Other	.476	.476	0	.476	3
FEET						0
HANDS	Lognormal	.276	16.9617	190.2144	.9801	12
TOTAL DERM:	27.1451	32.977	77.1476		27.1451	
INHALATION:	Lognormal	5.0678	5.1332	87.649	1.8802	20
COMBINED:	29.0253	38.0448	82.2808		29.0253	

95% C.I. on Mean: Dermal: (-923.6871, 1077.9823)

95% C.I. on Geo. Mean: Inhalation: (.033, 106.9864)

Inhalation Rate : 14 Liters/Minute
Number of Records: 20
Data File: MIXER/LOADER/APPLICATOR Subset Name: MOLINATE.MLAP